LOW-TEMPERATURE FUEL CELLS

1- PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFCs)

The PEMFCs were developed originally by General Electric in the 1960s for NASA’s space explorations. Over the years, these fuel cells have been known under various names, such as:

- *proton exchange membrane*
- *ion exchange membrane*
- *solid polymer electrolyte*
- or simply, *polymer electrolyte*.

They use hydrogen as fuel, oxygen or air as oxidant, and a solid polymer membrane as electrolyte.

Design Characteristics

The core of the PEMFC design consists of a proton conducting membrane (the electrolyte), located between two platinum-impregnated porous electrodes. Teflon gaskets and current collectors are added to these components to complete a single fuel cell unit. The core of the fuel cell is usually less than a millimeter thick and is referred to as the ***membrane-electrode assembly*** **(MEA)**. Depending on the mode of fabrication, MEA can include either the membrane along with the catalyst layers only, or the whole ensemble of the previously mentioned components plus the carbon electrodes. **Figure 1** shows a schematic representation of the PEMFC manufactured by Ballard Power Systems.

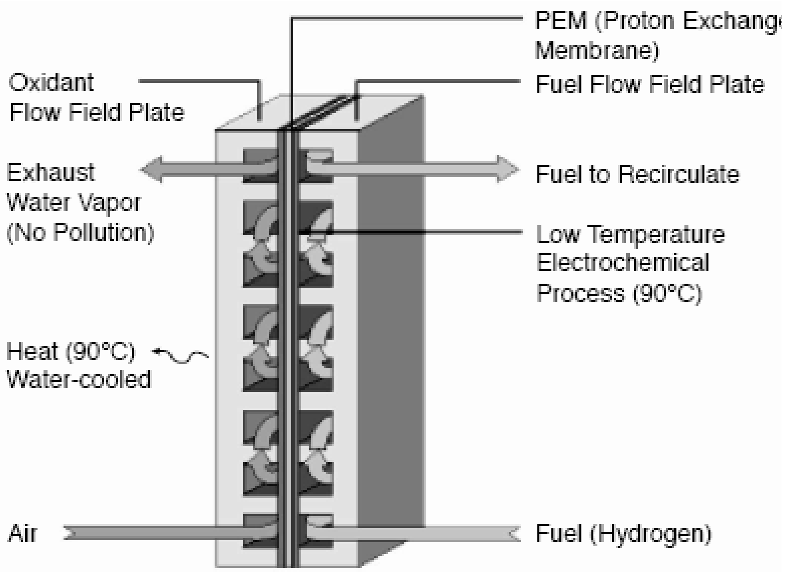


Figure 1: PEMFC, Ballard Power systems (From Ballard Power Systems, How the Ballard® fuel cell works).

A general view of the cell hardware and its cross section are presented in **Figure 2**.

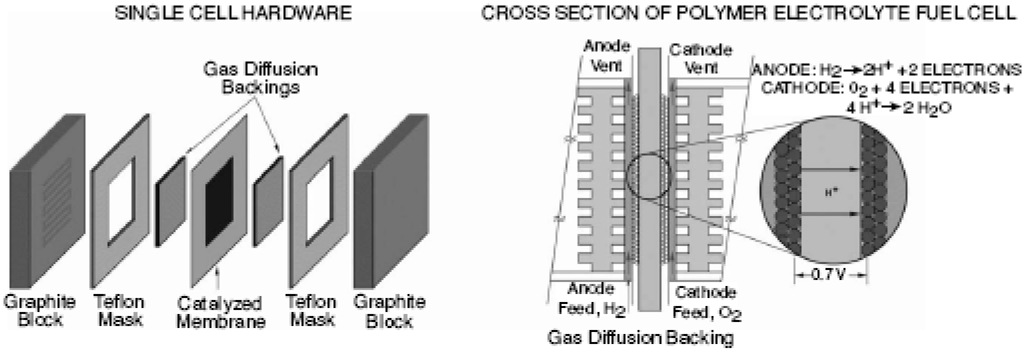


Figure 2: PEMFC design.

Electrolyte (membrane)

Various electrolyte materials have been developed over the years for use in PEMFC, and there is still extensive ongoing research focused on improving the materials currently used or finding new solutions. Currently, the thickness of the membrane is approximately 50–175 µm, and recent developments show that stable operation conditions can be obtained with membranes only 10–25 µm thick.

Most of the membranes used to date in PEMFC have a fluorocarbon-polymerbased structure to which sulfonic acid groups are attached. The key characteristic of these materials is that, although the acid molecules are fixed to the polymer, the protons on these acid groups are free to travel through the membrane. The most well known are the Nafion® membranes, which have been developed by DuPont over more than three decades. These types of membranes are thin, nonreinforced films based on the Nafion® resin, a perfluorinated polymer. The structure of the Nafion membranes is given in **Figure 3**.

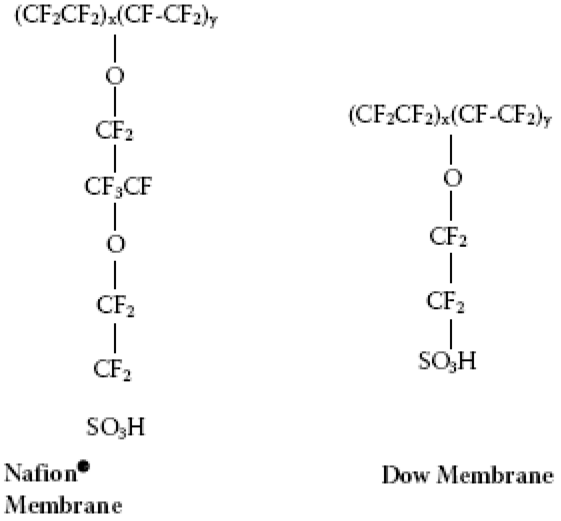


Figure 3: Structural characteristics of PEMFC membranes.

This type of membrane is usually prepared by modifying a basic polymer (polyethylene) through a process called *perfluorination*, where the hydrogen is substituted with fluorine. The modified polymer is the polytetrafluoroethylene (PTFE) or Teflon. A side chain of sulphonic acid HSO_3 is then added to PTFE through the “sulphonation” process. The end of the chain is an SO_3^- ion, and the HSO_3 group is ionically bonded. The resulting structure combines strong hydrophobic properties of the fluorocarbon polymer backbone with strong hydrophilic properties of the terminal sulfonic acid function. It is an excellent proton conductor, durable (owing to strong bonds between the fluorine and carbon) and shows good chemical resistance.

Tests showed that the PEMFC performance levels improved with the membrane developed by Dow Chemical. Although this membrane remains a perfluorosulfonic acid membrane, its structure is characterized by a shorter side chain and thus a lower equivalent weight compared to Nafion®. Conductivity and hydrophilic properties are slightly enhanced, and durability is still maintained. The Dow membrane was tested in 1987–1988 at Ballard Power Systems, and the results showed significant increases in PEMFC performance levels (**Figure 4**).

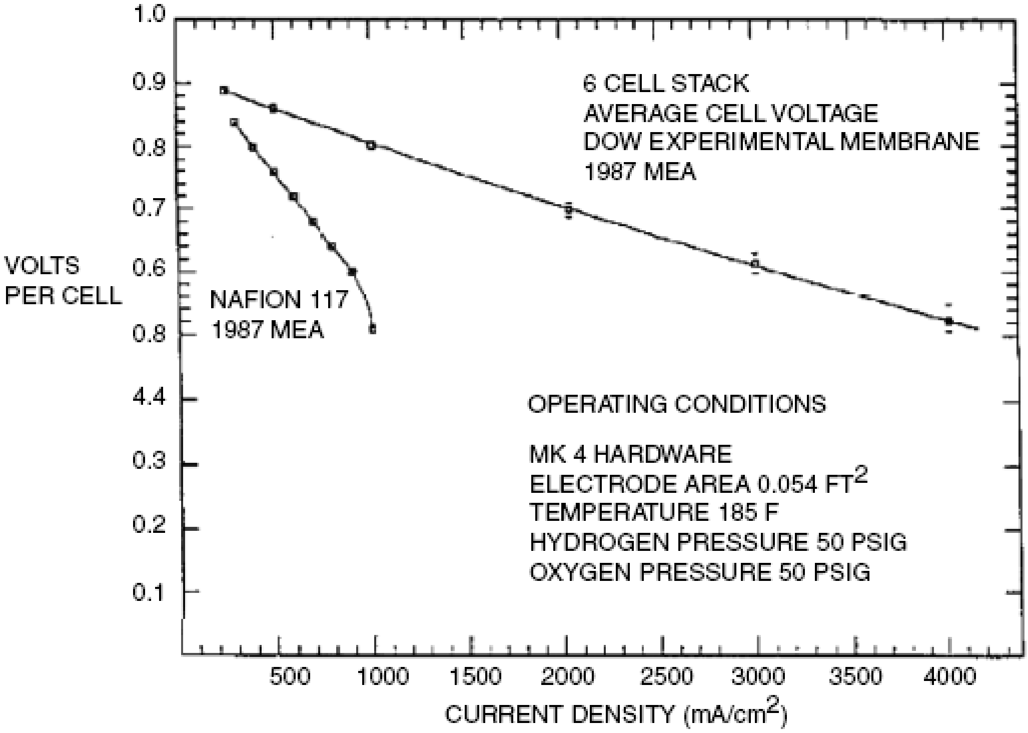


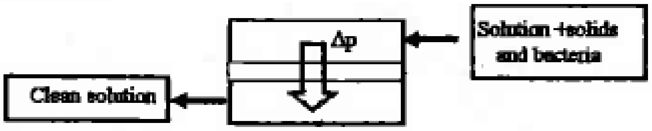
Figure 4: PEMFC performance using Nafion® and Dow membranes.

Ion exchange membranes

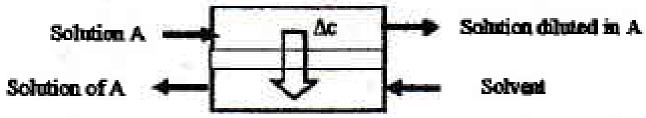
What is a membrane?

- Separator between two liquids
  Thin liquid film or more often organic polymer, ceramic or other inorganic material
- Natural membranes; animals & plants
- Synthetic membranes: 50 years,
  Chemical technology, biotechnology and environmental engineering
- Classified according to driving force
  Pressure difference, Concentration difference and Potential difference

- ΔP
  - Microfiltration, ultrafiltration, reverse osmosis, gas separation:

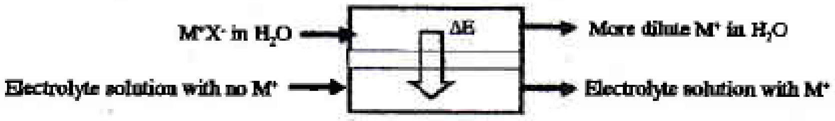


- Δc
  - Dialysis



and

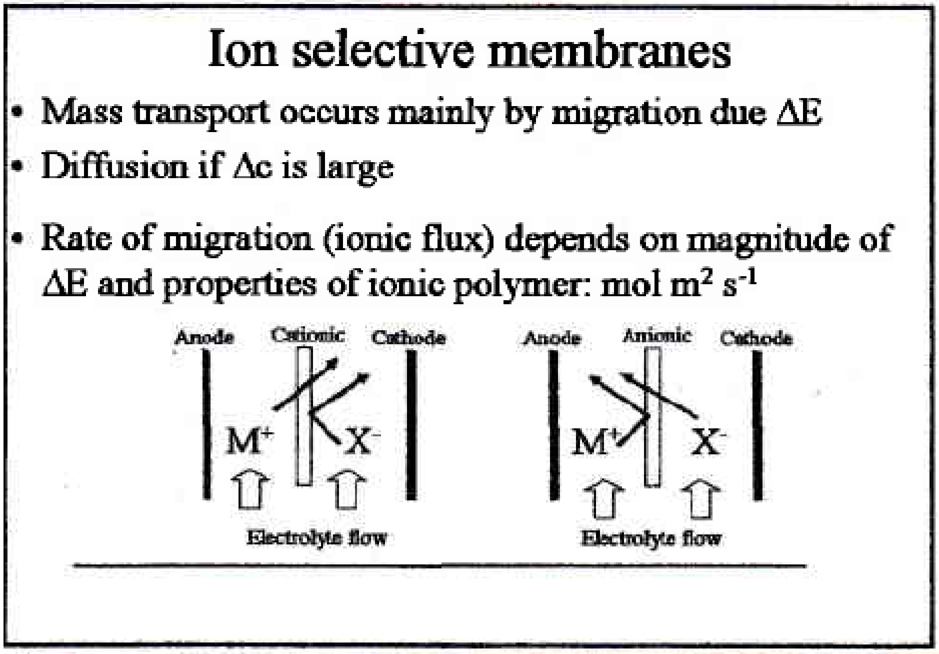
- ΔE
  - electrolysis, electro-dialysis, electrochemical process


M^+X^- in H_2O
ΔE
More dilute M^+ in H_2O
Electrolyte solution with no M^+
Electrolyte solution with M^+

Ideal separation:
High selectivity and fast rate

Ion selective membranes

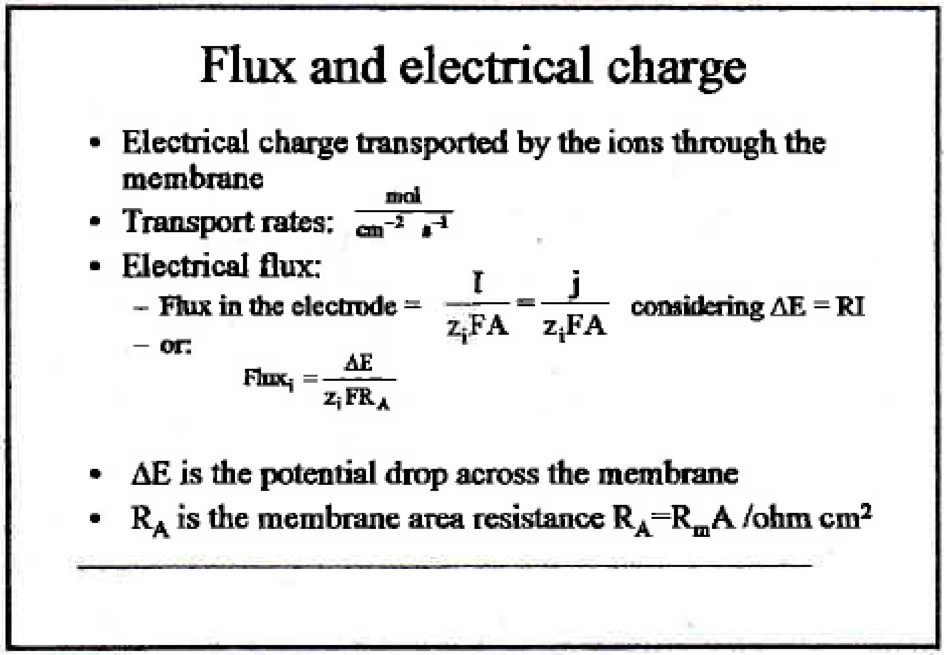
- Designed to pass selectively either cations or anions:
  Cationic allow positive ions
  Anionic allow negative ions
- Manufactured from organic polymers
  a) Styrene/divinylbenzene, high degree of cross linking
  b) Copolymers of perfluorinated alkene; linear polymers



Ion selective membranes

- Mass transport occurs mainly by migration due ΔE
- Diffusion if Δc is large
- Rate of migration (ionic flux) depends on magnitude of ΔE and properties of ionic polymer: mol m^2 s^{-1}

Anode
Cationic
Cathode
M^+
X^-
Electrolyte flow
Anode
Anionic
Cathode
M^+
X^-
Electrolyte flow



Flux and electrical charge

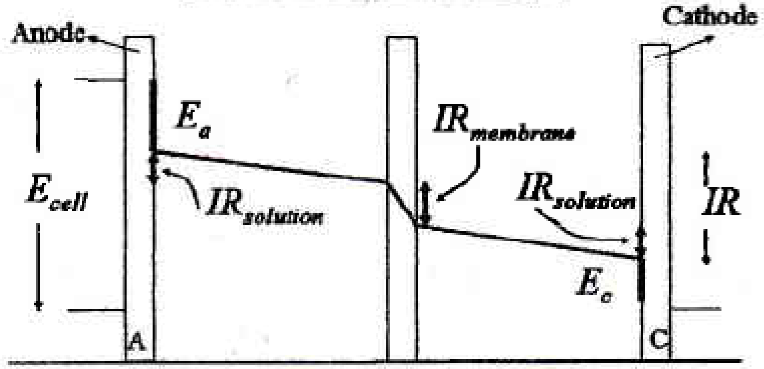
- Electrical charge transported by the ions through the membrane
- Transport rates: $\frac{\text{mol}}{\text{cm}^{-2}\ \text{s}^{-1}}$
- Electrical flux:
  - Flux in the electrode = $\frac{I}{z_i FA} = \frac{j}{z_i FA}$ considering $\Delta E = RI$
  - or:

$$\text{Flux}_i = \frac{\Delta E}{z_i F R_A}$$

- ΔE is the potential drop across the membrane
- R_A is the membrane area resistance $R_A = R_m A$ /ohm cm^2

Cell Voltage Components *vs.* Distance

$$\boxed{E_{cell} = E_c - E_a - IR}$$



$$\boxed{R = R_c + R_a + R_m}$$

Area resistance

- R_A related to ionic conductivity κ, of the membrane polymer, and its thickness L:

$$\boxed{R_A = \frac{L}{\kappa}}$$

- Transport number: fraction of the total charge carried through the membrane by a particular ion:
  - In a completely cation selective membrane: $t_+ = 1; \Sigma t_- = 0$
  - Typical values are 0.8 to 0.9

Example

- What is the conductivity of an electrolyte solution if the resistance was 1000 Ω measured in a cell with parallel electrodes of 1 cm^2 separated by 1 cm?

$$\boxed{R_A = \frac{L}{\kappa}}$$

$$\boxed{\kappa = \frac{L}{R_A} = \frac{L}{R\,A} = \frac{0.01\ \text{m}}{(1000\Omega)\ (0.0001\ \text{m}^2)} = 0.1\ \Omega^{-1}\text{m}^{-1} = 0.1\ \text{Sm}^{-1}}$$

Characterisation of ion exchange membranes

- Water content:

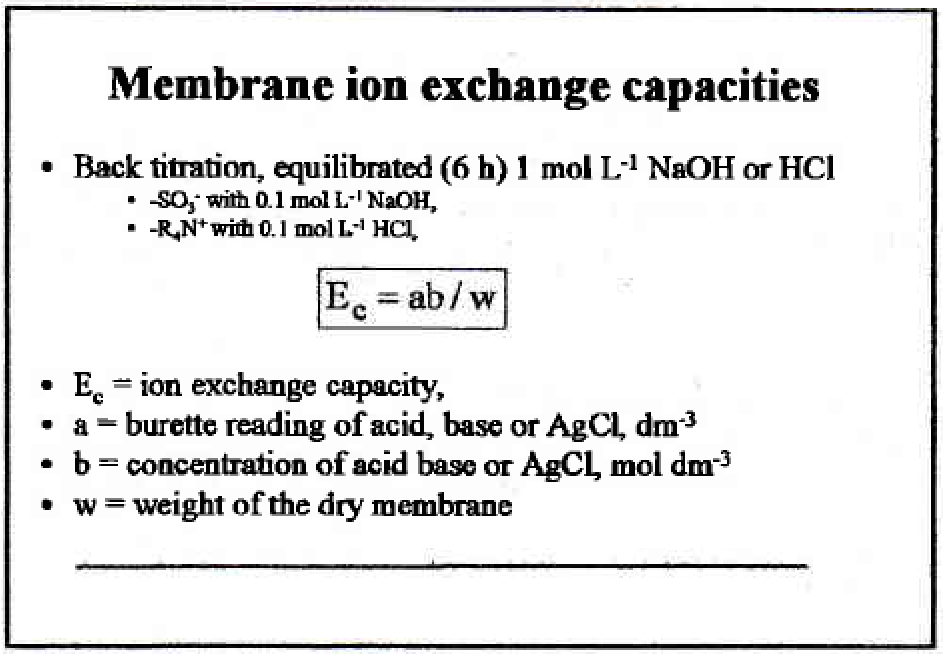
$$\boxed{C_w^m = (W_h - W_d)\ \rho_m / W_h M_W}$$

$C_w{}^m$ = concentration of water in the membrane,
W_h = weight wet membrane,
W_d = weight dry membrane,
ρ_m = the density of wet membrane
M_w = molar mass of water (18 g mol 1^{-1})

- Membrane porosity τ:

$$\boxed{\begin{array}{l} \tau = \Delta V/(1+\Delta V) \\ \Delta V = (W_h - W_d)\rho_d / \rho_w W_d \end{array}}$$

ΔV = volume increase due to absorption of water per unit of dry membrane volume,
W_h = weight of wet membrane,
W_d = dry membrane weight,
ρ_d = density of dry membrane,
ρ_w = density of water,

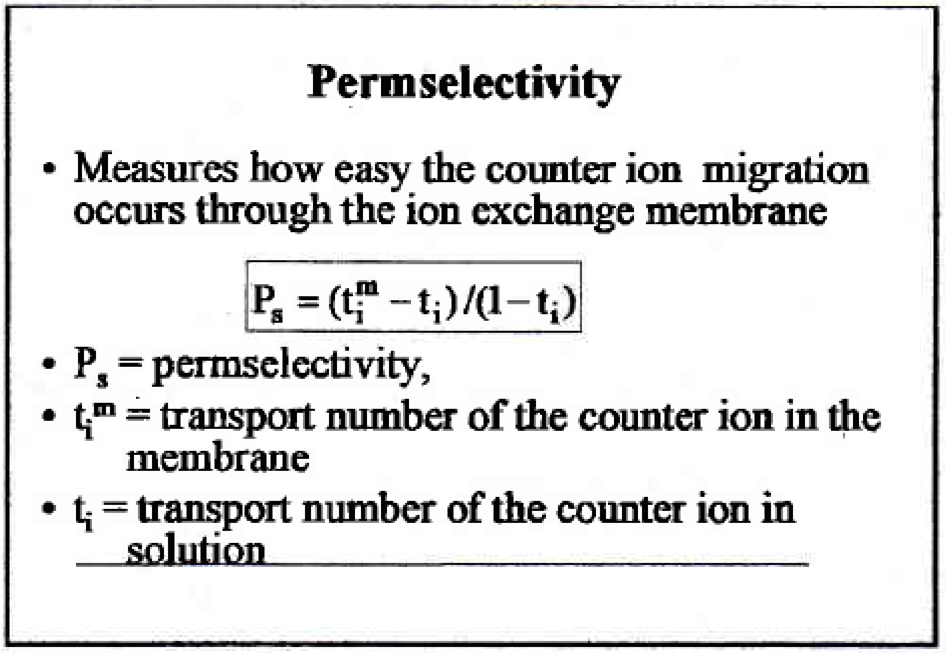


Membrane ion exchange capacities

- Back titration, equilibrated (6 h) 1 mol L^{-1} NaOH or HCl
    - $-SO_3^-$ with 0.1 mol L^{-1} NaOH,
    - $-R_4N^+$ with 0.1 mol L^{-1} HCl,

$$\boxed{E_c = ab / w}$$

- E_c = ion exchange capacity,
- a = burette reading of acid, base or AgCl, dm^{-3}
- b = concentration of acid base or AgCl, mol dm^{-3}
- w = weight of the dry membrane



Permselectivity

- Measures how easy the counter ion migration occurs through the ion exchange membrane

$$\boxed{P_s = (t_i^m - t_i)/(1 - t_i)}$$

- P_s = permselectivity,
- t_i^m = transport number of the counter ion in the membrane
- t_i = transport number of the counter ion in solution